

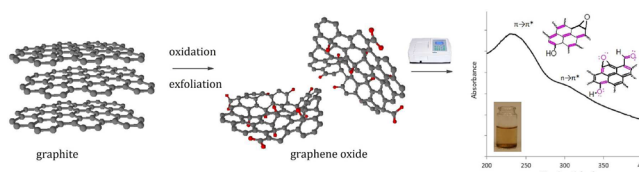
Graphene Oxide as Mine of Knowledge: Using Graphene Oxide To Teach Undergraduate Students Core Chemistry and Nanotechnology Concepts

Izabela Kondratowicz and Kamila Żelechowska

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

ABSTRACT: The aim of this laboratory experiment is to utilize graphene oxide (GO) material to introduce undergraduate students to many well-known concepts of general chemistry. GO is a new nanomaterial that has generated worldwide interest and can be easily produced in every well-equipped undergraduate chemical laboratory. An in-depth examination of GO synthesis, as well as a study of its structure and properties, allows students to familiarize themselves with the concepts of redox reactions, dispersity, and polarity, along with the basic concepts of spectroscopic methods. The inclusion of this carbonaceous nanomaterial within a basic chemistry curriculum can stimulate students' interest and introduce them to the modern field of nanotechnology. Students are tasked to prepare GO using the well-known improved Hummers' method. Then they study the dispersion behavior of GO and carry out Fourier transform infrared and UV–vis spectroscopic measurements to characterize the material. The experiments are designed to be accomplished in five 3-h sessions and have been successfully incorporated into the second-year undergraduate course at Gdańsk University of Technology over a three-year period.

KEYWORDS: *Second-Year Undergraduate, Interdisciplinary/Multidisciplinary, Hands-On Learning/Manipulatives, Nanotechnology, Oxidation/Reduction, UV–Vis Spectroscopy, IR Spectroscopy, Laboratory Instruction*



Graphene-like nanomaterials have gained much attention in recent years. Graphene is a monolayer of sp^2 -bonded carbon atoms arranged on a hexagonal lattice that resembles a honeycomb.^{1–3} Graphene oxide (GO) is a graphene layer decorated with oxygen-containing functional groups. It can be easily synthesized in the undergraduate student laboratory via the Hummers' method of graphite oxidation and its subsequent exfoliation using ultrasonication.^{4,5} During oxidation, oxygen-containing functional groups are introduced into graphene structure. It is known that carboxyl groups mainly occupy the edges of GO sheet, whereas epoxy and hydroxyl groups are introduced on the basal plane. The polar groups present in GO cause it to be more readily dispersed in polar solvents. The presence of different functional groups can be investigated by Fourier transform infrared (FTIR) spectroscopy.^{6,7} Moreover, some of these groups, for example, C=O or conjugated carbon–carbon double bonds, can also absorb light in the ultraviolet range. In this case, taking GO as an example, the ultraviolet and visible (UV–vis) spectroscopy technique and the Beer–Lambert law can also be employed.^{8–10} GO therefore serves as a versatile material to train undergraduates in the basic concepts of general chemistry.

In this experiment, students carry out the synthesis of GO using the improved Hummers' method and characterize the product by studying its dispersive properties in various solvents, and using FTIR and UV–vis spectroscopy. Students learn that GO possesses different oxygen functionalities that are introduced on graphite planes during the oxidation reaction.

They can then experimentally verify the properties of GO and understand the influence of solvent polarity on dispersion behavior. Students use FTIR and UV–vis spectroscopy to characterize the GO by determining functional groups present on the GO (qualitative determination). Finally, by using the Beer–Lambert law, they can calculate the absorptivity (α) of GO and test the long-term stability of GO water dispersions (quantitative determination).

The graphite rods from used zinc–carbon batteries or a natural graphite rock can be utilized here as a graphite source showing students the possibility of using everyday materials in the world of science. Introducing students to cutting edge areas of research, and using novel molecules such as GO to demonstrate fundamental chemistry concepts such as redox reactions, dispersion, infrared, and UV–vis absorption, can significantly increase their motivation and sense of achievement. Moreover, students will gain insight into handling a material that is the focus of a lot of current research in many fields. In addition, this practical course also strengthens their laboratory and communication skills as well as encourages teamwork.

■ PEDAGOGICAL GOALS

This laboratory experiment is aimed at accomplishing the following:

- To introduce undergraduates to basic concepts of chemistry using GO.
- To evaluate the chemical redox reactions occurring during the graphite oxidation.
- To understand the dispersion behavior of GO in terms of solvent polarity.
- To identify functional groups present on GO using FTIR spectroscopy.
- To qualitatively identify UV–vis light-absorbing groups using UV–vis spectrophotometry.
- To use UV–vis spectrophotometry quantitatively to test the long-term stability of GO aqueous dispersion and to determine the absorptivity of GO.

■ EXPERIMENTAL OVERVIEW

A detailed student handout is provided in the [Supporting Information](#). This experiment takes about 15 h, split into five weekly consecutive sessions of 3 h each, and can be one of the exercises in the one-semester laboratory course. It is designed for undergraduate students of nanotechnology or related fields (second or third year) within the “Nanochemistry”, “Chemistry of Nanomaterials”, or “Functional materials” laboratory. All students should have completed the introductory course of general chemistry before participating in this experiment. Moreover, basic laboratory skills are mandatory. Before laboratory work commences, 1 h should be devoted to teach students about the structural properties of graphene and GO. A short explanation of redox reactions, dispersion behavior, and polarity should be given. In addition, an introduction to spectroscopic methods (IR and UV–vis) is recommended. Students are also asked to write a theoretical introduction (maximum one A4-page long) prior to the experiments. At the beginning of the lab work, students are asked to study the handouts distributed by Teaching Assistant and to plan their experiments to fit into the lab sessions. Students prepare GO using the step-by-step procedures and complete all the tasks outlined in the handouts. Finally, they analyze all the data and write a report. Students are strongly recommended to discuss and share their findings with other groups as well as understand the scientific concepts of the experiment. After completion, students should be able to describe the properties of GO, its dispersion characteristics, presence of functional groups, and have an understanding of IR and UV–vis spectroscopic methods.

■ HAZARDS

Personal protective equipment (PPE) must be worn during the experiment: safety glasses, protective gloves, lab coat, long trousers, and covered shoes. All experiments should be carried out under fume hood. Potassium permanganate is a strong oxidizing agent and can react violently with a number of compounds. Any reactions with this compound should be carried out under controlled conditions and in an appropriate scale. Potassium permanganate is toxic to aquatic life with long lasting effects. Sulfuric and phosphoric acids are very hazardous in case of skin contact, of eye contact, of ingestion, and of inhalation. Sulfuric and phosphoric acids react violently with water. Always dilute acids by adding acid to water and not water to acid. Adding water to concentrated acid may cause violent

boiling of the solution and splashing. A mixture of concentrated acids should be added slowly and dropwise. Temperature should be maintained at about 5 °C during the oxidation of graphite as the reaction is highly exothermic. Additional attention should be paid when adding H₂O₂, as O₂ formed in the reaction causes intensive bubbling. The reaction mixture should be kept below 5 °C during this step, and H₂O₂ should be added in portions.

■ EXPERIMENTAL PROCEDURE

Before the laboratory session, students must attend a safety and chemical handling course. Students should be also familiar with all the chemicals they are going to use and be aware of hazards and precautions.

Materials and Equipment

Graphite flakes and potassium permanganate were purchased from Sigma-Aldrich. Instead of graphite flakes, graphite rods from used batteries or natural graphite block can be also used as a graphite source. Sulfuric acid (95%) and orthophosphoric acid (85%) were purchased from POCh Gliwice, Poland. Hydrogen peroxide (30%) was purchased from Sigma-Aldrich and diluted to 3%. Alternatively, it can be purchased in pharmacy. *N,N*-Dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane, and 1,2-dichlorobenzene were purchased from Sigma-Aldrich and used as solvents. DI water was used throughout the experiments. The experiments required a sonicator (Bandelin Sonorex), a centrifuge (Chemland D3024), an oil bath, ice bath, and a hot plate with magnetic stirrer (Heidolph MR Hei-Standard). For the characterization of GO, Frontier FTIR/FIR PerkinElmer and spectrophotometer Lambda 10, PerkinElmer were used. A digital camera may be helpful to take pictures of samples during the laboratory course. Vacuum dryer (Binder) was used to dry samples at lower pressure and temperatures.

Logistics

Timetabling of the experiments requires consideration of certain crucial steps in the process. The authors therefore suggest the following sequence. In Session 1, a theoretical introduction to spectroscopy and graphene materials should be covered (45 min lecture). At the end of this session, the oxidation of graphite, which requires 1.5 h, may be commenced in the lab and left overnight. The next day, the experiment should be stopped (hot plate and magnetic stirrer can be turned off by a teacher assistant) and the samples left until Session 2. Session 2 should be devoted to the continuation of GO production, washing, and centrifuging, which require 3 h. GO should be left to dry until the next session. During Session 3, the sonication of GO (2–3 h) should be carried out. In the meantime, students can broaden their theoretical knowledge or start working on their reports (e.g., prelab assessment, description of experimental part, etc.). During Session 4, the IR spectroscopic characterization of the GO could be undertaken followed by UV–vis spectroscopy in Session 5. In the meantime, the visual observation of GO suspensions could be made. Depending on the equipment availability, the order of Session 4 and 5 can be switched for certain students groups.

Preparation of GO

Students prepared GO using the improved Hummers' method.⁵ To start with, they mixed 0.2 g of graphite flakes with 1.2 g of KMnO₄. If graphite rods from used batteries or natural graphite block were used, students first crushed and ground them using



sandpaper and a mortar. As-prepared graphite powder requires several washes with DI water. The mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ in a volume ratio 9:1 (24 mL/2.7 mL) was then added slowly to graphite. An ice bath was used to keep the temperature below 5°C . The suspension so formed was left for 24 h with magnetic stirring. Then hydrogen peroxide 3% v/w was added, which resulted in a color change of the suspension to brown–yellow and formation of graphite oxide (GrO). The suspension was centrifuged at 15 000 rpm for 10 min and washed several times with DI water until the pH of the supernatant was neutral. It was then left to dry at room temperature or in a vacuum dryer as the detachment of oxygenated groups may occur at elevated temperatures. To obtain GO, the suspension of GrO powder in water (1 mg mL^{-1}) was sonicated for 3 h. The solid was separated by filtration or centrifugation and dried for further characterization.

RESULTS AND DISCUSSION

Visual Observations

Students were first asked to closely observe the graphite oxidation process and to make notes. During the experiment, several independent steps of GO formation can be distinguished by students. In the first step, graphite flakes acquire deep-blue color and so-called graphite intercalation compound (GIC) is formed. The suspension is green–purplish. Then the oxidation of GIC proceeds, and the purplish pasty suspension is formed.^{11,12} Addition of H_2O_2 causes the release of molecular O_2 in the form of bubbles,¹³ which thus terminates the whole oxidation process. The suspension changed color to yellow–brown, which confirms the successful formation of graphite oxide.

After the synthesis, students prepared GO suspensions in distilled water at concentration of 1 mg mL^{-1} . Then they were asked to visually note the properties of GO water suspensions. All students reported that the GO aqueous suspension was yellow–brown. The hydrophobic/hydrophilic properties of graphite and GO can be easily demonstrated by adding graphite and GO powder to water (Figure 1). The polar oxygen-containing groups in GO render it hydrophilic, contrary to graphite.¹⁴

Students then prepared GO suspensions in five different solvents: water, DMF, THF, dichloromethane, 1,2-dichlorobenzene (1 mg of GO per 1 mL of solvent). By comparing the polarity of solvents and their interactions with oxygen-

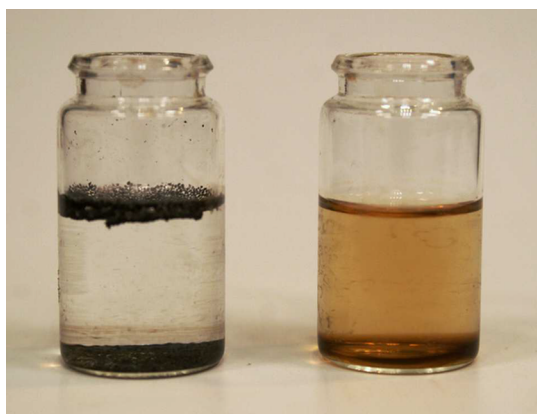


Figure 1. Comparison of graphite flakes (left) and GO water dispersions (right).

containing functional groups (via, i.e., hydrogen bonds) on GO plane,¹⁵ students learned about the relation between the dispersity of GO and solvent polarity. They recorded best dispersion in water and poorest dispersion in chloromethane and 1,2-dichlorobenzene.

FTIR Spectroscopy

FTIR spectroscopy is an analytical method routinely used in the organic chemistry laboratories. This method has been already described in the previous issues of this *Journal*^{6,16,17} and can be successfully implemented for analyzing nanomaterials including GO. Figure 2 shows the FTIR spectrum of graphite

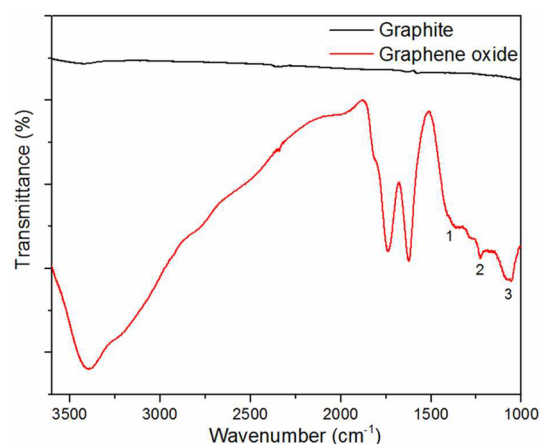


Figure 2. FTIR spectra of graphite and GO. 1, 2, and 3 numbers on GO spectrum correspond to bands at 1360 , 1225 , and 1060 cm^{-1} , respectively.

and GO obtained by students. No significant features appear on the graphite spectrum. Several bands however appear on GO. A distinct band at 1735 cm^{-1} confirms the presence of carbonyl groups. The small band at 1590 cm^{-1} is assigned to the stretching vibrations of $\text{C}=\text{C}$ conjugated with $\text{C}=\text{C}$ or $\text{C}=\text{O}$ bonds. Three bands at 1360 , 1225 , and 1060 cm^{-1} (marked as 1, 2, 3 on the graph) are placed in the region characteristic for stretching of $\text{C}-\text{O}$ bond in alcohols and epoxides. The presence of these new bands on GO spectrum is a confirmation of the successful oxidation.^{7,18} A strong, wide band centered at about 3390 cm^{-1} can be assigned to $\text{O}-\text{H}$ vibrations of water molecules adsorbed on GO. Since GO contains groups capable of creating hydrogen bonds with water molecules, the adsorbed water is difficult to remove and is revealed in the spectrum. As in the spectrum of graphite, no bands are present in this region, and it can be concluded that it is not the water adsorbed on used KBr.

UV–vis Spectrophotometry

UV–vis spectrophotometry can be used for qualitative as well as quantitative determination of compounds that absorb light in the ultraviolet and visible range. The UV–vis spectroscopy background was described in detail earlier.^{9,19} Thus, here we do not focus on the method itself, but we show its usefulness in GO analysis. As was shown by FTIR analysis in a previous subsection, GO contains carboxyl or carbonyl functional groups connected with $\text{C}=\text{C}$ bonds, which are also known to absorb light in the UV range. The obtained UV–vis spectra of GO aqueous suspensions are presented in Figure 3. The main maximum absorption band, observed at 230 nm , can be ascribed to $\pi \rightarrow \pi^*$ electron transition in conjugated carbon–

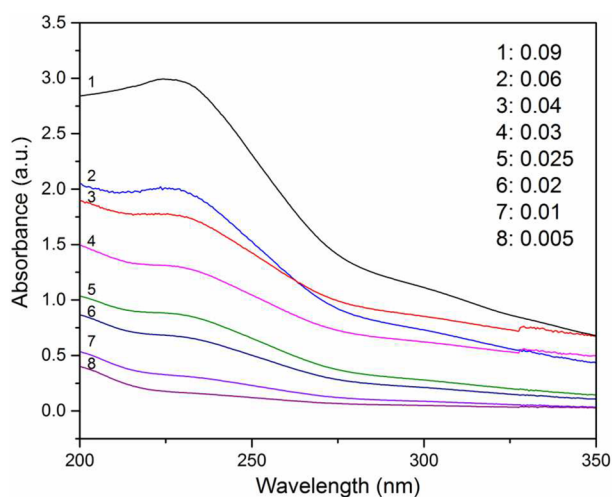


Figure 3. UV-vis spectra of GO water dispersion of different concentrations (in mg mL^{-1}).

carbon double bonds in the GO plane. The second, smaller band at 310 nm is connected with $n \rightarrow \pi^*$ transition of nonbonding electrons in oxygen atoms connected with double C=C bonds.¹⁰

For quantitative determination, a calibration curve (absorbance vs concentration) should be plotted. A representative calibration curve is shown in Figure 4. GO suspensions of

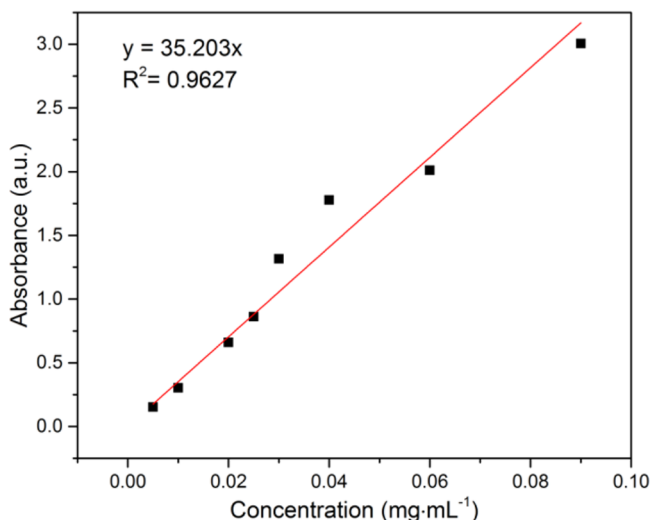


Figure 4. Calibration curve (absorbance vs concentration) for GO water dispersions.

different concentrations ranging from $0.005\text{--}0.09 \text{ mg mL}^{-1}$ were prepared by students. By utilizing the Beer–Lambert law⁸ and fitting a regression line to the obtained data, they successfully determined the absorptivity of GO suspension in water. The values were similar among all students groups. The correlation coefficient (R^2) obtained by students was about 0.9627, which is acceptable for the calibration curve of suspensions.

The suspensions were left undisturbed until the end of the laboratory course. Each group checked the stability of one chosen suspension in water. By knowing the absorptivity of GO, students calculated the new concentration of the chosen sample by running UV-vis absorption spectra and applying the

Beer–Lambert law. The decrease in sample concentrations was only around 6–10%, which confirmed good dispersion behavior of GO in water with almost no precipitation.

CONCLUSIONS

The integration of new carbon nanomaterials in the undergraduate chemistry course can be achieved by involving students with the experiments using GO, as practiced in many laboratories across the world. Hence, students are exposed to the real-world of nanoscience by getting a deeper understanding about redox reactions, dispersity, and polarity as well as the value of spectroscopic techniques. More than 400 undergraduate students of nanotechnology at the Gdańsk University of Technology completed the course with an average grade of 4.5 out of 5.5 over a three-year period. Students successfully obtained GO with the properties comparable to those reported in the literature. Students were fully motivated and excited according to a survey filled out prior to the laboratory. After the experiments, students were asked about their opinions and feedback, and 80% of the students felt the experiments met their expectations and kept them engaged throughout the whole course. Most of them were astounded at upcycling spent carbon–zinc batteries and hence contributed positively to environmental issues.

This experiment produced desired results by leaving students with a binding impression and profound knowledge of the explored topics. The experiment was easy to perform and successful in engaging second-year undergraduate students with basic laboratory skills.

REFERENCES

- (1) Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S. Graphene based materials: Past, present and future. *Prog. Mater. Sci.* **2011**, *56*, 1178–1271.
- (2) Liu, J.; Xue, Y.; Zhang, M.; Dai, L. Graphene-based materials for energy applications. *MRS Bull.* **2012**, *37*, 1265–1272.
- (3) Park, S.; Ruoff, R. S. Chemical methods for the production of graphenes. *Nat. Nanotechnol.* **2009**, *4* (4), 217–224.
- (4) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80* (6), 1339–1339.

- (5) Marcano, D. T.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. *ACS Nano* **2010**, *4* (8), 4806–481.
- (6) Pimentel, G. C. Infrared Spectroscopy: a Chemist's Tool. *J. Chem. Educ.* **1960**, *37* (12), 651–657.
- (7) Kondratowicz, I.; Żelechowska, K.; Sadowski, W. Nanoplasmonics, Nano-Optics, Nanocomposites, and Surface Studies. *Springer Proc. Phys.* **2015**, *167*, 167–467.
- (8) Swinehart, D. F. The Beer-Lambert Law. *J. Chem. Educ.* **1962**, *39* (7), 333–335.
- (9) Erhardt, W. Instrumental Analysis in the High School Classroom: UV–Vis Spectroscopy. *J. Chem. Educ.* **2007**, *84* (6), 1024–1026.
- (10) Lai, Q.; Zhu, S.; Luo, X.; Zou, M.; Huang, S. Ultraviolet-visible spectroscopy of graphene oxide. *AIP Adv.* **2012**, *2* (3), 032146.
- (11) Whitener, K. E.; Sheehan, P. E. Graphene synthesis. *Diamond Relat. Mater.* **2014**, *46*, 25–34.
- (12) Dimiev, A. M.; Tour, J. M. Mechanism of graphene oxide formation. *ACS Nano* **2014**, *8* (3), 3060–3068.
- (13) Sun, L.; Fugetsu, B. Mass production of graphene oxide from expanded graphite. *Mater. Lett.* **2013**, *109*, 207–210.
- (14) Wang, G.; Wang, B.; Park, J.; Yang, J.; Shen, X.; Yao, J. Synthesis of enhanced hydrophilic and hydrophobic graphene oxide nanosheets by a solvothermal method. *Carbon* **2009**, *47*, 68–72.
- (15) Konios, D.; Stylianakis, M. M.; Stratakis, E.; Kymakis, E. Dispersion behavior of graphene oxide and reduced graphene oxide. *J. Colloid Interface Sci.* **2014**, *430*, 108–112.
- (16) Wilson, K. W. Student experiments in infrared spectroscopy. *J. Chem. Educ.* **1953**, *30* (7), 340–342.
- (17) MacCarthy, P.; Bowman, S. J. Undergraduate infrared spectroscopy experiments. *J. Chem. Educ.* **1982**, *59* (9), 799–801.
- (18) Singh, V. K.; Patra, M. K.; Manoth, M.; Gowd, G. S.; Vadera, S. R.; Kumar, N. In situ synthesis of graphene oxide and its composites with iron oxide. *New Carbon Mater.* **2009**, *24* (2), 147–152.
- (19) Moeur, H. P.; Zanella, A.; Poon, T. An Introduction to UV-Vis Spectroscopy Using Sunscreens. *J. Chem. Educ.* **2006**, *83* (5), 769.

